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Flavonoid Glycosides from the Pinnae of *Lunathyrium japonicum*

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ABSTRAK

Penyelidikan semula terhadap flavonoid glikosida dari spesies L. japonicum *telah menunjukkan kehadiran kuersetin 3-O-rutinosida, visenin-2, kaemferol glikosida dan viteksin. Oleh yang demikian flavonoid data dari kajian ini kelihatan berbeza (kecuali penemuan viteksin) dengan data yang diperolehi oleh Hiraoka (1978). Perbezaan corak flavonoid di antara* L. japonicum *dari Jepun dengan* L. japonicum *dari Semenanjung Malaysia, mencadangkan variasi geografi. Lanjutan dari pengekstrakan flavonoid dari pinna-pinna* L. japonicum *dalam kajian ini juga mendapati kuersetin 3-O-rutinosida dan visenin-2 dilapurkan pertama kalinya dijumpai dalam famili Athyriaceae.*

ABSTRACT

Reinvestigation of the flavonoid glycosides of the species L. japonicum *indicated the presence of quercetin 3-O-rutinoside, vicenin-2, kaempferol O-glycosides and vitexin. Thus, the flavonoid data at present seem to be different(except for the presence of vitexin) from those of Hiraoka (1978). The differences in flavonoid patterns between* L. japonicum *from Japan and* L. japonicum *from Peninsular Malaysia suggest geographical variation. In addition to the extraction of flavonoids in* L. japonicum *in the present study, quercetin 3-O-rutinoside and vicenin-2 were reported for the first time in the family Athyriaceae.*

INTRODUCTION

Previous flavonoid studies on *Lunathyrium japonicum* (Thunb.) Kurata (Hiraoka 1978) revealed the presence of vitexin, orientin, kaempferol 3-*O*-glucoside and quercetin 3-*O*-glucoside in the pinnae. Reinvestigation of the flavonoid glycosides of the species *L. japonicum* in the present study established that the major flavonoid glycosides in this fern are quercetin 3-*O*-rutinoside, vicenin-2, unidentified kaempferol *O*-glycosides but besides vitexin.

MATERIALS AND METHODS

Plant Sources

Fern samples were collected from the natural habitat in Malaysia. A voucher specimen was deposited in the herbarium at the Botany Department, University of Reading, Berkshire, England (collector No. U174). Fresh grown samples were supplied by Kew Garden, Surrey, England. The fern samples were air-dried before extraction. Dried pinnae (3 g) were homogeneously powdered.

Identification of Flavonoids

Two-dimensional paper chromatographic surveys of pinnae were carried out using the solvent pairs; *n*-BuOH-HOAc-H_2O (4:1:5) (BAW) and 15% HOAc. R_fs, UV spectral analysis and colour reaction with and without ammonia for the compounds, run one-dimensionally by descent on Whatman No. 1 paper, are given in Table 1. Known flavonoid glycosides were identified by standard procedures (Harborne 1967) and in most cases compared directly with authentic samples. Flavonoid aglycones were identified in acid hydrolysed pinnae extracts using standard procedures (Harborne 1967) by comparison with authentic markers.

TABLE 1

Spectral and Rf properties of flavonoid glycosides of *Lunathyrium japonicum*

Glycoside	Absorption spectrum (nm) in MeOH				R_f(x100) in			Colours in UV	
	Alone	+NaOAc	$+H_3BO_3$	+NaOH	BAW	H_2O	15%HOAc	PhOH	Alone	$+NH_3$
Qu 3-*O*-rutinoside	253,263sh. 354	271	374	410	51	47	50	34	dark	yellow
Vitexin	270,338. 279	380	398	39	11	20	61		dark	yellow
Vicenin	271,336. 276	350	400	68	17	37	76		dark	yellow

BAW, *n*-BuOH-HOAc-H_2O (4:1:5, top layer); PhOH-H_2O (4:1); sh. = shoulder.

RESULTS AND DISCUSSION

On acid hydrolysis, both samples of *L. japonicum* produced cyanidin and quercetin. The alcoholic extracts produced quercetin 3-*O*-rutinoside but in the fresh-grown sample of *L. japonicum*, unidentified kaempferol *O*-glycosides, vitexin and vicenin-2 were detected. However, these glycosides were not found in dried samples of the field collection. This may be due to variations in the chemistry between the two populations of *L. japonicum*, or due to differences in fresh and dried plant material. The former possibility seems more likely, since most flavonoids are stable and will not be destroyed on drying. Furthermore, Hiraoka (1978) studied the same species and found a different flavonoid pattern again. *L. japonicum* appears to show interspecific chemical variation. Hiraoka found vitexin, orientin, kaempferol 3-*O*-glucoside and quercetin 3-*O*-glucoside in the frond extracts of the species. The differences in flavonoid patterns between *L. japonicum* from Japan and Malaysia suggest geographical variation. Wollenweber (1982) also encountered this phenomenon when he analysed the flavonoids in the fronds of *Cheilanthes farinosa* (Polypodiaceae). In the samples from Africa, he found kaempferol 3,7,4'-tri-*O*-methyl ether, kaempferol 7,4'-*O*-dimethyl ether, methyl ether of quercetin, kaempferol 7-*O*-methyl ether and apigenin 7,4'-*O*-dimethyl ether. In the samples from Asia, the same derivatives of kaempferol were present, in addition to kaempferol 3,7-*O*-dimethyl ether. In *C. argentea*, there also seemed to exist a correlation between geographical and flavonoid composition. The specimens from Japan produced an unidentified diterpene and a series of new flavanones (Wollenweber *et al.* 1980). Those from China produced the same diterpene but none of the new flavanones. The samples from Taiwan were distinguished very clearly by production of a different unknown diterpene and possibly one of the new flavanones (Dietz 1980). A similar observation has been made in *C. anceps*. The flavonoid pattern in samples from the northern part of India appears to be different from that of material from the south of India (Wollenweber 1982). These findings, however, are still to be confirmed by analysis of further samples from the different regions.

Quercetin 3-*O*-rutinoside has previously been found from the leaf of *Ruta graveolens* (Rutaceae) (Harborne 1967). Vicenin-2 has been found before in bryophytes (Mues and Zinsmeister 1976;

Osterdahl 1979) and ferns (Wallace *et al.* 1981). However, these flavonoids are reported for the first time in the Athyriaceae. Further flavonoid studies on other taxa of this family are in progress.

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